STRUCTURAL CHARACTERIZATION

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Research on the synthesis and structural characterization of a wide variety of materials continues. Some highlights of this period follow:

An exact description has been formulated for the stress field, deformation field, and swelling distribution around an idealized filler particle in an elastomer.

A new organic compound, 1,3-butanediol-3-acetate, has been prepared for the first time as part of the preparation of low-molecular-weight analogs of poly(vinyl acetate/vinyl alcohol) copolymers.

By measurements of diffusion coefficients, it is estimated that the effective valence of aluminum dissolved in zinc single crystals is closer to +2 than the expected +3.

Several sets of energetic calculations are in agreement with the proposal that the stable interstitial complex formed when a chlorine molecule is introduced in NaCl or KCl consists of the neutral Cl_2 molecule occupying adjacent structural voids along a [100] direction.

ANELASTIC AND DIELECTRIC RELAXATION IN POLYMERS

Senior Investigator: R. K. MacCrone

Anelastic and dielectric measurements on polystyrene and poly(methyl methacrylate) have been made at low temperatures. These measurements show several distinct relaxation processes in the 4 - 30K temperature range. The temperatures at which the relaxations are a maximum occur roughly at the temperatures T_E of the Einstein modes of frequency $w_E (= kT_E/\hbar)$ introduced to explain the excess specific heat observed in these materials (G. Salinger, private communication). It is hypothesized that the structural entities responsible for the anelastic and dielectric relaxations are also responsible for the excess specific heat.

On the assumption that the vibration of a structural entity in the polymers may be approximated by a simple harmonic oscillator, a theoretical analysis is presented which shows that dielectric and anelastic relaxations will occur provided the harmonic oscillator is charged and coupled to the bulk strain through a Grüneisen constant.

The most difficult quantity to evaluate is the relaxation time τ and its temperature dependence, since this depends on the details of the interactions between the structural entity and the bulk phonons. A very crude estimate suggests that $\tau = \tau_o \exp(\hbar w_E/kT)$, and this expression is not inconsistent with the experimental observations.

Dielectric measurements on polybutene show no relaxations in this temperature region. Since this polymer exhibits no excess specific heat, the lack of dielectric relaxations is taken as good confirmation for the hypothesized origin of the relaxations in polystyrene and poly(methyl methacrylate).

POLYMER-SOLVENT INTERACTIONS

Senior Investigator: S. S. Sternstein

I. Inhomogeneous Swelling in Filled Elastomers

The most frequently used technique for measuring crosslink density in elastomers is the swelling method, the validity of which rests on an accurate description of both the thermodynamics of polymer-solvent interactions and the network strain energy function. In filled elastomers an added complication is the inhomogeneity of the swelling in the vicinity of the filler particles.

An exact description of the deformation field, stress field, and swelling distribution in the vicinity of an isolated, spherical filler particle has been obtained for completely general polymer-solvent interactions and stored energy function (which is an arbitrary function of the three strain invariants). Specific calculations have been performed for polymer-solvent interactions obeying the Flory-Huggins theory and a neo-Hookean strain energy function. Typical results are shown in Figures 1 and 2 for a particular value of χ and crosslink density and a rigid filler particle. In Figure 1, the deformation field is shown as a function of distance from the filler particle surface. The associated stress field is shown in Figure 2. Clearly, the inhomogeneous swelling due to the contraint imposed by the filler particle is pronounced.

The stress field results are being used to determine the birefringence which a filled, swollen system would exhibit, and experimental verification is in progress. Additional calculations

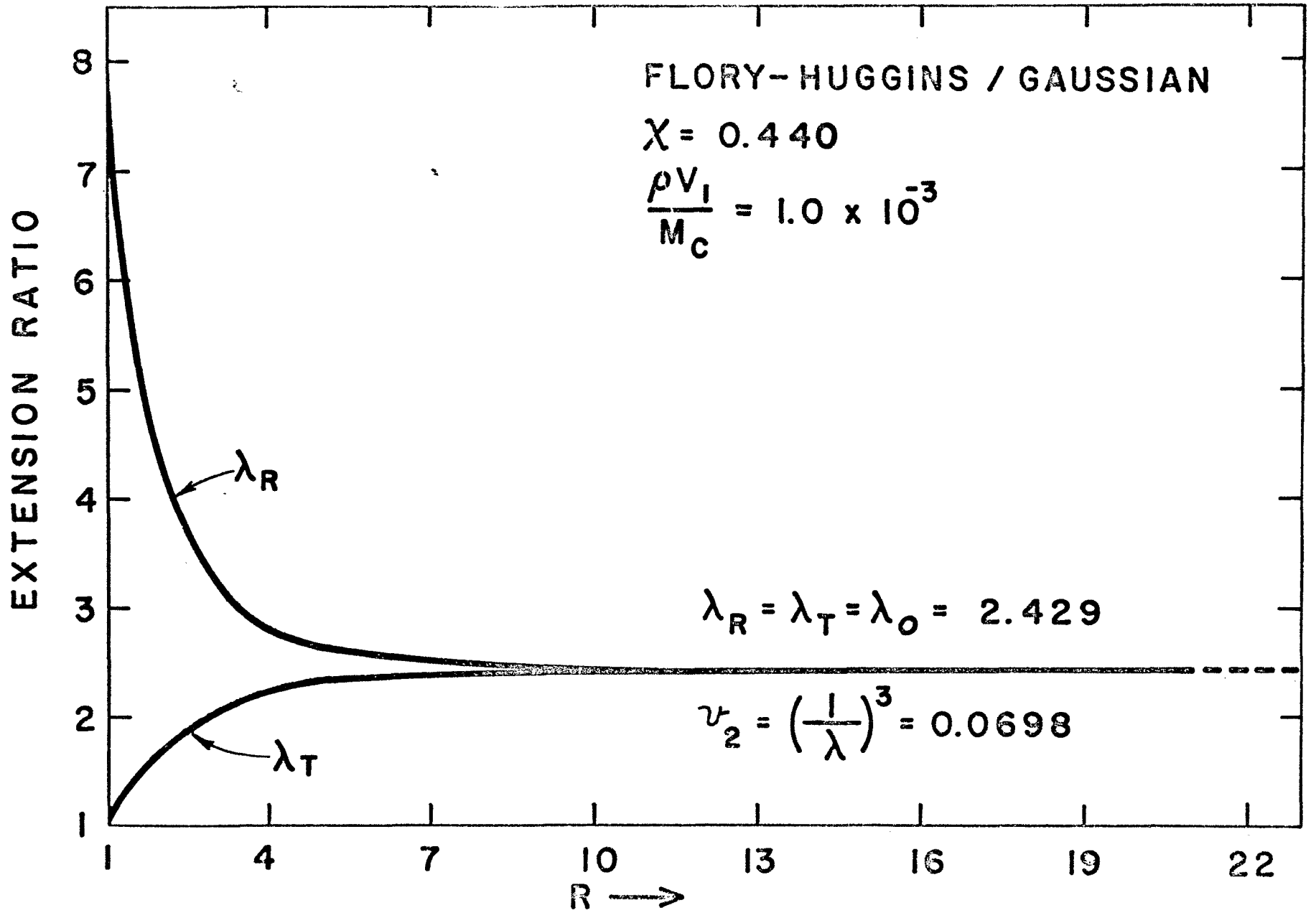
FLORY-HUGGINS / GAUSSIAN
χ = 0.440
ρV1/Mc = 1.0 x 10^-3
EXTENSION RATIO
λR
λT
λR = λT = λo = 2.429
ν2 = (1/λ)^3 = 0.0698
R ⟶
1
4
7
10
13
16
19
22
1
2
3
4
5
6
7
8

FIGURE 1

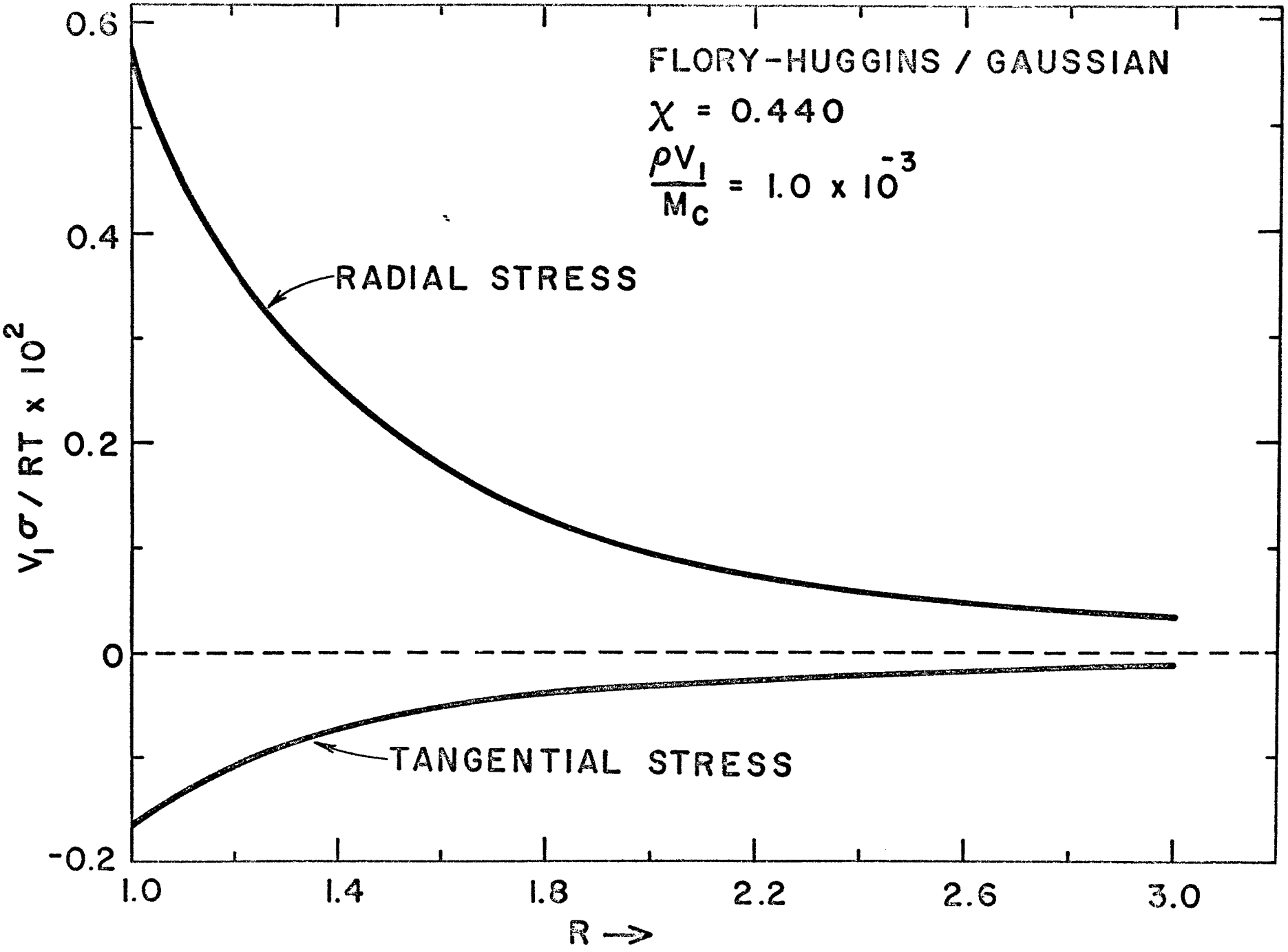
FLORY-HUGGINS / GAUSSIAN
χ = 0.440
ρV1/Mc = 1.0 x 10^-3
RADIAL STRESS
TANGENTIAL STRESS
V1σ / RT x 10^2
R →
0.6
0.4
0.2
0
-0.2
1.0
1.4
1.8
2.2
2.6
3.0

FIGURE 2

on interfacial stresses and deformations are being performed, as well as the tabulation of swelling errors and correction factors to be applied to swollen, filled elastomers to compensate for the interfacial swelling diminution.

II. Constant Volume Polymer-Solvent Interactions

The constant volume cell described previously has now been modified to allow equilibrium to be established between an elastomer sample held at constant volume and the pure swelling agent at arbitrary pressure. Special samples have been obtained for this study and include random copolymers of styrene and butadiene and of acrylonitrile and butadiene, both of various compositions. These samples, together with the previous data on natural rubber, will provide information on the effects of cohesive energy density and polarity on the "swelling pressure." It is also planned to study filled elastomer systems in an attempt to determine the efficiency of matrix-filler adhesion and the resultant immobilization of interfacial rubber.

SOLUTION PROPERTIES OF POLYMERS

Senior Investigator: S. Krause

The study of the lowest molecular weight analogs of vinyl acetate vinyl alcohol copolymers has continued. Before studying the solution properties of these copolymers, we intend to investigate carefully the circumstances under which random and block copolymers are formed from vinyl acetate homopolymer and from vinyl alcohol homopolymer. We have continued our work with 1,3-butanediol and 2,4-pentanediol.

Both monoacetates and the diacetate of 1,3-butanediol have been prepared, purified, and characterized by means of high resolution NMR and gas chromatographic techniques. The work has been complicated by the fact that the 3-acetate of 1,3-butanediol has not previously been reported in the literature. It appears to have the same boiling point, refractive index, and behavior in the gas chromatograph as the 1-acetate, but the high resolution NMR spectrum is different. Additional proofs of structure will be necessary since the infrared and NMR spectra of these model compounds will be used later to analyze the structures of the copolymers.

The optical isomers of 2,4-pentanediol have been separated by means of ion exchange of their borate complexes. The meso-isomer is the lowest molecular weight analog of isotactic poly(vinyl alcohol) while the d and ℓ isomers are analogs of syndiotactic poly(vinyl alcohol). Many ion exchange runs will have to be made in order to obtain workable amounts of these isomers, so

that we can again prepare mono- and diacetates as model compounds. These isomers will also be used to study the rates of esterification as a function of tacticity. Rates of saponification and of methanolysis of the diacetates will also be studied as a function of tacticity.

LOW-ANGLE LIGHT SCATTERING STUDIES

Senior Investigator: F. W. Billmeyer, Jr.

Our low-angle light scattering photometer is being used to measure the molecular weights of various samples of DNA. The goal of the project is to measure and compare the molecular weights of samples of DNA taken from normal and neoplastic human tissue, in order to determine whether any real differences between corresponding samples do exist.

At present, we are making instrumental modifications that will facilitate the measurement of absolute scattering intensities with our low-angle photometer. These include improvements in some of the optical and mechanical components as well as changes in the size and shape of the scattering cell. Upon completion of these modifications, the instrument will be calibrated using absolute turbidity standards, such as "Ludox" silica sols and solutions of 12-tungstosilicic acid, to obtain absolute scattered intensities. Once the instrument has been so calibrated, it will be used in conjunction with our conventional wide-angle photometer (previously calibrated in a like manner) to study the full range of angular scattering of the DNA samples.

With the wide-angle photometer, we have been working with a sample of calf-thymus DNA, the accepted molecular weight standard for most work with DNA, in order to acquaint ourselves with the procedures involved prior to examining the same sample on the low-angle instrument.

THERMODYNAMICS OF POLYMER SOLUTIONS

Senior Investigator: F. W. Billmeyer, Jr.

Studies continue upon the system polybutene-1/toluene using the three samples described previously. It has been determined that 50°C is the lowest convenient temperature at which to conduct these investigations with any assurance of complete sample dissolution.

Results are now complete for the dilute-solution osmometry at 50°C utilizing the Stabin High Speed Osmometer. Experiments are still required at two successively higher temperatures. Viscosity determinations also are almost complete.

The examination of the three polybutenes at 50°C by vapor sorption is complete. Consideration of the vapor sorption isotherms indicates that at this temperature it is most likely that only the totally amorphous region participates in solvent adsorption. Agreement between solvent sorption and evacuation isotherms for the samples supports the hypothesis that the crystalline regions contribute negligibly at this temperature.

It is believed that at higher temperatures solvent will penetrate increasing fractions of the "ordered" regions. It is expected that there will be lack of agreement between the two isotherms due to the formation of form III polybutene from the original form I sample. Additional sorption experiments will be initiated in an effort to further elucidate the relative stabilities of the two forms and the characteristics of the form I to III transformation.

One additional experiment is presently under consideration; i.e., the volume change on mixing polybutene with toluene. Using this information, plus data from dilatometry (already obtained here) and literature data available, one can analyze the vapor sorption and dilute solution results presently being obtained by means of the new and powerful free-volume theory of the thermodynamics of polymer solutions recently presented by Flory. [P. J. Flory and B. E. Eichinger, Trans. Faraday Soc., 64, 2035, 2053, 2061, 2066 (1968); P. J. Flory and J. L. Ellenson, Macromolecules, 1, (3), 279, 285, 287 (1968)].

CHARACTERIZATION OF NARROW DISTRIBUTION POLYMERS

Senior Investigator: F. W. Billmeyer, Jr.

One of the most difficult tasks in the molecular characterization of polymers is the determination of the breadth of the molecular-weight distribution in narrow-distribution samples - by which we mean polymers with $\overline{M}_w/\overline{M}_n$ less than, say, 1.10. We are applying the summative fractionation method described by Billmeyer and Stockmayer, J. Polymer Sci., 5, 121 (1950), to the solution of this problem for commercially-available narrow-distribution polystyrenes with $1.02 < \overline{M}_w/\overline{M}_n < 1.10$. The method has seldom been actively used for many years, but the earlier studies suggested that it should have unusually good sensitivity in this region, which is otherwise not experimentally accessible without excessively large errors.

We are developing semi-micro techniques, anticipating later application of the method, if feasible, to a "super-narrow" distribution polystyrene with $\overline{M}_w/\overline{M}_n \simeq 1.005$, of which we have been given 60 milligrams, a substantial fraction of the total supply ever prepared!

BORON FILAMENT DEPOSITION

Senior Investigator: R. J. Diefendorf

Work on boron filament production using a carbon substrate, previously described in these reports, continues with the objectives of elucidating the processes occurring during the deposition and determining the processing conditions required to produce high-quality filament.

STRUCTURAL AND PHASE STUDIES OF INORGANIC MATERIALS

Senior Investigator: H. Wiedemeier

The objectives of this work are to study solid state phase equilibria and transformations of inorganic materials with technologically interesting properties. Trends in recent years indicate a growing need for mixed compositions of AB compounds. It is, therefore, of practical importance to investigate the structural properties of such alloys.

As a continuation of previous studies, the system manganese selenide - cadmium selenide is now under investigation. Manganese selenide exists in several crystallographic modifications, the stable one being the NaCl-type structure. The d-level of the Mn atom is half filled. The stable modification of cadmium selenide at room pressure is the wurtzite-type structure; the NaCl-type structure of CdSe can only be obtained through the application of high pressure. The cadmium d-level is completely filled. These differences in structural and electronic properties of the components are the decisive quantities for the type of phase diagram to be established.

The pure compounds MnSe and CdSe were synthesized by vapor transport reactions with iodine as a transport agent. Chemical analysis and x-ray diffraction patterns verified that both materials were stoichiometric and had the NaCl and wurtzite structure, respectively. For the preparation of solid solutions powdered mixtures of MnSe and CdSe in various molar ratios were compressed into pellets, sealed under high vacuum in quartz ampules, and annealed at temperatures

between 500° and 1100°C. To ensure equilibrium, all samples are subjected to repeated annealing cycles until the cell dimensions of the phases present remain constant. Debye-Scherrer x-ray diffraction techniques are used to establish the phases in equilibrium. The degree of solid solution is determined from the change in lattice parameter with composition and the appearance of the second phase. Debye-Scherrer photographs are obtained in a 114.59 mm camera with Ni-filtered CuKα-radiation. Lattice parameters for compositions in the cubic phase region are calculated by the extrapolation method using high angle reflections only. For the evaluation of lattice parameters of compositions in the hexagonal phase region the reciprocal lattice method is used.

Preliminary results indicate the presence of a cubic and hexagonal one-phase region, separated by a wide two-phase area. The back reflection lines of the x-ray patterns become more diffuse with increasing solid solution. Extensive annealing is required to improve the crystallinity of the alloys in order to obtain sharp and well-resolved diffraction patterns for precise determinations of lattice constants and phase boundaries.

STRUCTURAL CHARACTERIZATION OF AND WITH ZINC SINGLE CRYSTALS

Senior Investigator: H. M. Gilder

I. Impurity Diffusion Rates

The diffusion of aluminum in zinc single crystals is being studied as a function of both temperature and crystal orientation in an attempt to understand the effective valence of aluminum ions dissolved in zinc. Aluminum atoms are labeled by use of the radioisotope Al^{26}. After the isotope is electrodeposited on a surface of a zinc specimen and diffused into the bulk, the specimen is sectioned with a lathe and each section assayed for radioactive content with a gamma-ray coincidence spectrometer. This allows a determination of the rate at which the aluminum penetrates the zinc.

Diffusion coefficients (or diffusion rates) for aluminum in zinc have been measured at temperatures of $350^{o}C$ to $400^{o}C$ along the two principal symmetry directions of zinc. By comparing the diffusion rate of aluminum in one principal direction with its diffusion rate in the other, we estimate that the effective valence of aluminum dissolved in zinc is closer to 2^{+} than 3^{+}.

Since large amounts of aluminum must be diffused in zinc to detect the Al^{26}, a certain amount of alloying occurs during the diffusion process. This very much complicates the interpretation of the data. We are, therefore, presently trying to develop techniques that will allow much smaller amounts of aluminum to be used.

II. Thermal-Expansion Measurements of Vacancy Formation Parameters

We are measuring the thermal equilibrium concentration of point defects (such as vacancies) in zinc, as well as the kinetics of their formation. The contribution that crystal defects make to the thermal expansion of the crystal is detected when extremely accurate measurements of the thermal expansion are made up to near the melting point. The measurements are made in a specially-designed vacuum furnace having viewing ports that enable surface markers to be followed with precision micrometer microscopes.

There appears to be a systematic departure from the ideal crystal thermal expansion at high temperatures in both principal symmetry directions of the zinc lattice. Present results indicate large inward displacements parallel to the c axis of atoms surrounding vacancies, and possibly a large anisotropy in the rearrangement of atoms during the process of vacancy formation. The "extra" volumetric expansion at high temperatures indicates a vacancy energy of formation of $0.5 \pm .05$ eV and entropy of formation of $(2.3 \pm .5)$ k.

We intend to supplement the present "macroscopic" measurements of length change with x-ray measurements of the lattice parameter changes

QUANTITATIVE ELECTRON MICROPROBE MICROANALYSIS TECHNIQUES

Senior Investigator: G. Judd

The research efforts in this project have been divided into two main areas: the modification and adaptation of existing computer programs to quantitative electron probe microanalysis techniques and the study of the electron beam characteristics in the electron microprobe with a correlation of inherent beam characteristics to x-ray intensity, backscattered electron current, and secondary electron current generation.

The Microprobe Analysis General Intensity Correction Program (MAGIC) developed by Dr. Colby of Bell Laboratories was modified for use on the RPI IBM 360-50 computer for Fortran G compiling. This program is now being used to process the raw data from the electron probe microanalyzer. This program was modified to increase the speed of the data handling, improve some of the correction procedures, and increase its versatility by allowing various entry points into the program. A plotting program was also added to the main computer program as a subroutine.

The characteristics of the electron beam study was undertaken to determine precisely the electron density within the electron beam of the microprobe and its effect on the generation of secondary electrons, primary backscattered electrons, and characteristic x-ray intensities as recorded in the detection instrumentation. A complete characterization of the beam characteristics will yield a better understanding of the meaningful resolution limits of this type

of instrumentation. It should also provide data for lowering the resolution limits by using a computer analysis of generated intensity data. This experiment involves scanning the beam across a highly polished right angle of conducting metal, thereby causing an abrupt change in the material concentration with which the beam interacts. Analysis of the generated intensity output as a function of beam position relative to the discontinuity can then yield the initial electron density distribution in the beam. An aluminum edge, a gold edge, and an aluminum to gold interface are the samples currently being investigated.

In addition to these studies, the facility itself has been used extensively by other research groups and has provided both research and training capabilities in electron probe microanalysis.

NUCLEAR MAGNETIC RESONANCE

Senior Investigator: P. A. Casabella

The study of the polarizability of the ions in solid alkali halides is nearly complete. The experiments consist of studying the nuclear magnetic resonances of the nuclei in single crystals of these materials while under a uniaxial strain. Experiments have been completed on NaF, NaCl, NaBr, KCl, and KBr. However, the first attempts to explain the measurements in terms of existing theories were not completely satisfactory. The approach has now been modified, and the calculations have been carried out with contracted free ion electron wave functions. Physically it is to be expected that the wave functions should contract when the ions are placed in solids, but the size of the contraction is not easy to calculate. In this work, the contraction was adjusted to agree with the experimental magnetic susceptibility. The ionic polarizability calculated with these contracted wave functions give far better agreement with the experimental results than did the earlier calculations. It seems clear that this approach is correct and only leaves the question of whether a better method of determining the contraction factor can be found.

ELECTRON SPIN RESONANCE

Senior Investigator: A. C. Greene

Studies of defect formation and energetics in the alkali halides have been continued. Emphasis has been directed towards examination of interstitial halogen complexes, particularly the neutral Cl_2 molecule in KCl and NaCl. For comparison purposes we have also studied the energetics of the H-center, a Cl_4^{3-} molecular ion complex occupying three adjacent lattice ion sites along a [110] direction. The energetics which include determination of lattice strain, polarization, and molecular binding energies have been calculated using an energy minimization technique.

Several approaches have been utilized. First, energies were calculated using published repulsive interaction (Fumi-Tosi) parameters for ion-ion repulsion between nearest neighbors only. The energies associated with interstitial molecular formation in an otherwise perfect crystal were computed to be 3.1 eV for NaCl and 1.7 eV for KCl. The energies associated with H-center formation were 1.8 eV for NaCl and 2.4 for KCl. In the latest approach, Hartree-Fock ionic wave functions were modified to fit diamagnetic susceptibility data and then used to compute the repulsive energy parameters. An excellent fit to the Fumi-Tosi parameters was obtained when effects of both first and second nearest neighbor repulsion were included. With second neighbor interactions taken into account, the molecular Cl_2 energies are 2.9 eV for NaCl and 1.1 eV for KCl, while the H-center energies are 1.7 eV in NaCl and 2.2 eV in KCl.

These results support the proposal that the stable interstitial complex consists of the Cl_2 molecule occupying adjacent structural voids along a [100] direction. The energy associated with the Cl_2 is computed to be lower than that of two isolated H-centers. The proposed mechanism for the Cl_2 formation consists of H-center diffusion along [110] directions at temperatures in excess of 77K and subsequent H-H annihilation at close distances to form the more stable Cl_2 complex.

X-RAY STUDIES OF HARD TISSUES AND BIOMATERIALS

Senior Investigator: J. L. Katz

The motivation in these areas has been to determine and understand the basic relationships between the structures of various hard tissue components (hydroxyapatite, collagen, amorphous calcium phosphate, ACP) and the function, behavior and properties of bone and teeth in the body. This is then used as the reference for the design and development of prosthetic and/or restorative materials for these hard tissues.

To this end, an extensive series of experiments has been instituted to study the physical properties of various apatites, collagen, whole bone, ACP, amalgams, alloys, ceramics, as well as some other minerals which occur in non-mammalian biological systems such as shell fish.

The x-ray experiments have involved several techniques:

Diffraction by Polycrystalline Systems:

X-ray measurements have been used to:

1. Categorize phase changes in amalgams and their constituent alloys due to pressure.

2. Identify the amount of ACP vs. hydroxyapatite in the bone samples being studied. The profiles of the hydroxyapatite peak are used to study recrystallization as well as to estimate the degree of crystallization (particle size, perfection) present in the sample.

3. Obtain the diffraction pattern for ACP. This has then been used as the basis for calculating the structural configuration and co-ordination of the calcium and phosphate groups in a glassy ensemble.

Pole Figure and Fiber Orientation Methods:

The computer-controlled automated full-circle diffractometer has been adapted for use in experiments to determine the orientation of collagen fibers and hydroxyapatite crystallites in oriented samples of bone and teeth. This information will be used in correlative studies of the elastic, mechanical and fracture properties of these tissues.

Small-Angle Scattering Methods:

These techniques have been used both for orientation and crystallinity studies of long-chain biological molecules (such as collagen and muscle fibers) and for particle-size studies of bone mineral and ACP.

In addition, there is under construction a set-up for determining elastic and mechanical properties of systems such as collagen and muscle fibers while under continual small- and wide-angle x-ray scattering observations. These data will be correlated with the results of the pole figure and fiber orientation studies mentioned above.

Supplementing these x-ray techniques are a series of experiments involving other instrumentation which has been made available through the IMRC facility with the assistance of other senior investigators.

Measurements of the elastic properties of bone, teeth, amalgams, alloys and various apatites has continued using ultrasonic techniques. In addition, the pressure-dependent elastic behavior of these materials has also been studied using the solid-media pressure apparatus coupled with an ultrasonic interferometer.

Studies of the surfaces of amalgams, alloys and bone specimens have been performed using electron microscopy and microprobe techniques in order to study the distribution of phases in these systems.

Infrared spectroscopy has been used as an adjunct to the x-ray powder techniques in order to characterize the mineral and bone apatite samples.

A system for measuring electrical conductivity in mineral and bone apatite polycrystalline samples was designed and constructed. This system permits measurements as a function both of pressure and temperature.

The conductivities as well as the activation energies calculated for anion diffusion are listed in the table below for various apatites.

Material	Conductivity, $(ohm\text{-}cm)^{-1}$	Activation Energy, eV
OH Apatite	3.3×10^{-11}	0.9
F Apatite	2.6×10^{-13}	1.1
Cl Apatite	1.4×10^{-12}	1.1
Bone Mineral	$< 10^{-14}$	-

In the theoretical area, calculations of the elastic properties of amalgams as composites and bone as a two-phase composite are still in progress.

X-RAY STUDIES OF LATTICE DYNAMICS

Senior Investigator: J. L. Katz

Experimental studies on new systems in this area have been temporarily suspended during Dr. Katz's sabbatical leave. The present activities are concerned mainly with checking out the computer-controlled automated diffractometer system for such studies on a fully automatic basis.

In the theoretical area calculations of thermal diffuse scattering contributions to integrated x-ray intensities have been expanded to include a more exact method of determining the contributions from elastic constant data. It is believed that comparison of these results with our earlier model calculations and the calculations of Skelton and Katz, Cooper and Rouse, and Walker and Chipman will aid in setting up more realistic force models for crystals.